Report for 2002SD2B: Lipid Geochemistry of Waters and Sediments in a Prairie Pothole Hydrologic System

There are no reported publications resulting from this project.

Report Follows:

Problem and Research Objectives

The Big Sioux aquifer is a shallow groundwater system that supplies water to many municipalities and rural, domestic wells in eastern South Dakota. The aquifer has large storage capacity and very rapid recharge characteristics (1).

Until recently, water quality studies of the Big Sioux aquifer, and the Big Sioux Basin, have focused on the inorganic constituents of the waters. We have conducted a geochemical baseline survey of the aquifer's organic constituents that has shown that dissolved organic carbon (DOC) levels within the aquifer are low, averaging 7.7 mg DOC/L (2). However, we have found that DOC levels in wetlands, lakes and rivers that are hydrologically connected to the aquifer can be as much as 30 times higher. The relatively low levels of DOC in the system suggest that it may be a sensitive indicator of the groundwater's quality. Thus it is vital that the organic geochemistry of this system be understood and modeled.

While we are currently investigating the nature of the humic component of the DOC in the aquifer, and the flux of organic carbon between hydrologic domains (e.g., between surface water and the groundwater, or between soil water and the ground water), the effect of selective sorption of the lipid component (compounds such as fatty acids, fatty alcohols, hydrocarbons, etc.) on the chemical characteristics of the groundwater's DOC to subsurface and aquifer material as it moves from one hydrologic domain to the other, is unknown. This is particularly important since we have shown that natural sorbents such as sand, aluminum oxides and clay minerals can selectively sorb different chemical components of a water's DOC (3, 4, 5).

This proposal addresses two major priorities identified by the Water Resources Research Institute's Regional Competitive Grants Program in their solicitation. First, this study addresses the issue of ground and surface water quality. It fills a significant gap in the knowledge of the water quality of the Big Sioux aquifer by quantifying the DOC flux through the system and identifying sorptive reactions with subsurface materials that control lipid concentrations and geochemistry in the aquifer system. Second, it will investigate the relationship and connections between surface water and groundwater DOC and how the lipid components of the DOC contribute to the movement of organic carbon through each hydrologic domain. Since many organic contaminants (such as pesticides, herbicides, PCBs, or PAHs) rapidly and intimately associate with the organic coatings on mineral surfaces, knowledge of the lipid geochemistry will provide information that may be important in predicting organic contaminant fate and transport in this system. This study will provide a missing portion of the geochemical understanding of organic carbon movement that is necessary to manage this resource, protect the groundwater's quality from degradation from anthropogenic organic substances, and if one day needed, facilitate its remediation.

The comprehensive objectives of this project are to: 1) identify the solvent extractable organic compounds (ie, lipids) present in the water and sorbed to the sediments and aquifer materials using gas chromatography mass spectrometry; 2) perform sorption/desorption experiments using representative lipids (natural and model compounds) and sediment and aquifer materials (minerals isolated from cores and reference mineral specimens) to quantify the binding of lipids to mineral surfaces; 4) assess the importance of sorption to mineral surfaces as mechanism for controlling lipids in the aquifer, and; 5) identify the nature and mechanism of lipid binding to the sediment and aquifer material particle-surfaces suing solid-state NMR and small-angle x-ray and light scattering.

This report covers the second year of what has been proposed as a three-year study whose goal is a comprehensive understanding of the lipid geochemistry of the Big Sioux Aquifer. Completing Objective 1 was the focus of this project year.

Methodology

This site consists of self-contained, permanent/semi-permanent pothole wetland around which we have installed a field of 17 nested groundwater wells. We have recently developed a hydrologic model for this site using MODFLOW (6). The site's geology and hydrology are described in detail by Sumption (6). Dissolved organic carbon from the pothole, the groundwater and water-soluble organic carbon from the surrounding soil were fractionated using XAD-8 and XAD-4 resin columns in series. Hydrophobic and hydrophilic neutral components were isolated after desorption of the acid and base fractions from the columns.

Organic matter samples were characterized by ultrafiltration and quantitative ^{13}C solid-state DPMAS NMR and fluorescence spectroscopies.

Principal Findings and Significance

The hydrophobic and hydrophilic neutral fractions from each environment exhibit unique characteristics compared to other organic matter fractions in the system. The fluorescence and quantitative ^{13}C solid-state DPMAS NMR spectra clearly distinguish between the neutral fractions organic matter fractions. The hydrophobic and hydrophilic neutral fractions from each environment are distinct organic matter fractions. The neutral fractions are lower molecular weight materials than the other organic matter fractions. Their quantitative NMR spectra display distinct carbon type distributions that distinguish them from the other organic materials. The hydrophobic neutrals are more aliphatic than the hydrophobic neutrals. The neutral fractions fluoresce more strongly and at different wavelengths than any of the other organic matter fractions. The molecular weight data, fluorescence and quantitative ^{13}C solid-state DPMAS

NMR spectra also clearly distinguish between the neutral fractions from the groundwater, pothole surface water and water-soluble organic carbon. This indicates that even though there is a hydrologic connection between the surface and ground waters, there are mechanisms that cause the groundwater's neutral components to differentiate themselves from the surface waters (pothole and water-soluble organic carbon in the soil).